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(54) **ALKALINE SECONDARY BATTERY**

(57)Abstract:
PROBLEM TO BE SOLVED: To suppress the increase of an internal pressure at the time of overcharge and overdischarge by using polytetrafluoroethylene with specified molecular weight for the binding agent of the negative electrode of an alkaline secondary battery and specifying the specific surface area of the conductive agent of the negative electrode.
SOLUTION: In an alkaline secondary battery comprising a positive electrode 2, a negative electrode 4, a separator 3 installed between the positive electrode 2 and the negative electrode 4 and an alkaline electrolytic solution, a material containing the polytetrafluoroethylene having average molecular weight of 20×104 to 100×104, the polytetrafluoroethylene having average molecular weight of 200×104 to 1000×104 and the other polymer is used for the binding agent of the negative electrode. For a conductive material of the negative electrode, a material containing as a main body a carbon black having a specific surface area of not less than 700m2/g is used. It is preferable that the polytetrafluoroethylene having average molecular weight of 20×104 to 200×104 of approximately 0.1 to 2.1 parts by weight is added to a hydrogen storage alloy powder of 100 parts by weight, and also it is preferable that the polytetrafluoroethylene having average molecular weight of 200×104 to 1000×104 of approximately 0.9 to 2.0 parts by weight is added thereto.

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CLAIMS

[Claim(s)]

[Claim 1] In the alkali rechargeable battery equipped with the separator infixed between the negative electrode which consists of a conductive substrate with which it filled up with the paste containing a positive electrode, a hydrogen storing metal alloy and a binder, and an electric conduction agent, and said positive electrode and said negative electrode, and the alkali electrolytic solution As for the binder of said negative electrode, the polytetrafluoroethylene and the mean molecular weight of 200,000-1 million contain [a mean molecular weight] the polytetrafluoroethylene of 2 million-10 million. And the electric conduction agent of said negative electrode is an alkali rechargeable battery characterized by specific surface area making a subject the carbon black 700m2 / more than g.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the alkali rechargeable battery equipped with the paste type hydrogen storing metal alloy negative electrode which improved the binder and the electric conduction agent.

[0002]

[Description of the Prior Art] The nickel hydrogen rechargeable battery which is an example of an alkali rechargeable battery has the structure which contained in the container the electrode group which infixed the separator between the positive electrode containing the nickel hydroxide which is an active material, and the negative electrode containing hydrogen storing metal alloy powder, and was produced with the alkali electrolytic solution. In said rechargeable battery, capacity of a negative electrode is usually enlarged compared with the capacity of a positive electrode. If said rechargeable

battery is made overcharge, charge of a positive electrode will be completed previously and oxygen gas will occur from said positive electrode. For this reason, prevention of internal pressure lifting at the time of overcharge is in drawing by returning said oxygen gas to water by the three-phase zone of the interface of the part in which the alkali electrolytic-solution layer of the hydrogen storing metal alloy powder front face of said negative electrode is formed, and the part in which the alkali electrolytic-solution layer is not formed, i.e., a gaseous phase, the liquid phase, and solid phase. On the other hand, if said rechargeable battery is made into overdischarge, hydrogen gas will be generated from the positive electrode which discharge ended previously. Prevention of internal pressure lifting at the time of overdischarge is in drawing by oxidizing by said three-phase zone of said negative electrode, and changing this hydrogen gas into water.

[0003] By the way, said negative electrode adds a water soluble polymer binder and polytetrafluoroethylene, and electric conduction agents, such as polyacrylate, for example, to hydrogen storing metal alloy powder, after it kneads it under existence of water and it prepares a paste, applies said paste to conductive substrates, such as punched metal, and is manufactured by drying and rolling out. Since such a negative electrode contains a water soluble polymer binder, the alkali electrolytic solution tends to permeate. Therefore, since the whole hydrogen storing metal alloy powder front face was covered in an alkali electrolytic-solution layer, said negative electrode of a three-phase zone was lost, and the rechargeable battery equipped with said negative electrode had the trouble that internal pressure rose, at the time of overcharge and overdischarge.

[0004] Since it is such, in order to secure reinforcement, paying attention to the polytetrafluoroethylene added by the negative electrode having high water repellence, raising water repellence and making a three-phase zone increase is performed by making [many] the amount of the polytetrafluoroethylene under said paste, or applying the suspension of polytetrafluoroethylene on the surface of a negative electrode.

[0005] However, if the amount of polytetrafluoroethylenes in a negative electrode is made [many], in order for the fluidity and adhesiveness of a paste to fall remarkably, the spreading nature to the conductive substrate of a paste is spoiled remarkably.

[0006] Since it was difficult to raise the water repellence of the interior on the other hand when applying polytetrafluoroethylene to a front face and producing a negative electrode, it was difficult at the time of overcharge and overdischarge to fully control internal pressure lifting of said rechargeable battery. Furthermore, in order that a water-repellent-finish process might increase, there was a trouble that the fabrication operation of said rechargeable battery became complicated.

[0007] By the way, as an electric conduction agent of said negative electrode, acetylene black, metal powder, etc. are known conventionally. However, since the amount of insulating polytetrafluoroethylene was increased, the negative electrode to which water repellence was given by approach which was mentioned above was difficult to fully raise the flow of hydrogen storing metal alloy powder by such electric conduction agent. Consequently, since electric resistance becomes large as for said negative electrode, as for the rechargeable battery equipped with said negative electrode, a high current discharge property falls. Moreover, although the method of raising the flow of comrades in the end of an alloy powder by covering a hydrogen storing metal alloy powder front face with a metal membrane was learned instead of adding such an electric conduction agent to a paste, the production process of a negative electrode became complicated and

there was a trouble that a manufacturing cost soared.
[0008]
[Problem(s) to be Solved by the Invention] The object of this invention is offering the alkali rechargeable battery which the charge-and-discharge property in a high current is improved, and internal pressure lifting at the time of overcharge and overdischarge is controlled, and can produce a negative electrode by the easy approach by improving a binder and an electric conduction agent.
[0009]
[Means for Solving the Problem] The negative electrode with which the alkali rechargeable battery of this invention consists of a conductive substrate with which it filled up with the paste containing a positive electrode, a hydrogen storing metal alloy and a binder, and an electric conduction agent, In the alkali rechargeable battery equipped with the separator infixed between said positive electrodes and said negative electrodes, and the alkali electrolytic solution the binder of said negative electrode A mean molecular weight is characterized by specific surface area making [the polytetrafluoroethylene and the mean molecular weight of 200,000-1 million] a subject the carbon black 700m2 / more than g, as for the electric conduction agent of said negative electrode, including the polytetrafluoroethylene of 2 million-10 million.
[0010] Hereafter, the example of the alkali rechargeable battery (cylindrical shape alkali rechargeable battery) concerning this invention is explained with reference to drawing 1 . In the container 1 of the shape of a closed-end cylinder which serves as a negative-electrode terminal as shown in drawing 1 , the electrode group 5 produced by carrying out the laminating of a positive electrode 2, a separator 3, and the paste type negative electrode 4, and winding in the shape of a spiral is contained. Said negative electrode 4 is arranged at the outermost periphery of said electrode group 5, and touches said container 1 electrically. The alkali electrolytic solution is held in said container 1. The circular obturation plate 7 which has a hole 6 in the center is arranged at up opening of said container 1. The insulating ring-like gasket 8 is arranged between the periphery of said obturation plate 7, and the up opening inner surface of said container 1, and is fixing said obturation plate 7 to said container 1 airtightly through said gasket 8 by caulking processing which reduces the diameter of said up opening inside. An end is connected to said positive electrode 2, and, as for the positive-electrode lead 9, connection and the other end are connected to the underside of said obturation plate 7. The positive-electrode terminal 10 which makes a hat configuration is attached so that said hole 6 may be covered on said obturation plate 7. The relief valve 11 made of rubber is arranged so that said hole 6 may be closed in the space surrounded with said obturation plate 7 and said positive-electrode terminal 10. The pressure plate 12 which consists of an insulating material which has a hole in the center is arranged so that the height of said positive-electrode terminal 10 may project from said hole on said positive-electrode terminal 10. The sheathing tube 13 has covered the periphery of said pressure plate 12, the side face of said container 1, and the pars-basilaris-ossis-occipitalis periphery of said container 1.
[0011] Next, said positive electrode 2, the paste type negative electrode 4, a separator 3, and the electrolytic solution are explained.
1) a positive electrode 2 -- electric conduction material is added to the nickel compound which is an active material, it kneads with a binder and water and a paste is prepared, this positive electrode 2 fills up a conductive substrate with said paste, and after drying, it is

manufactured by fabricating.
[0012] As said nickel compound, nickel hydroxide, a nickel oxide, etc. can be mentioned, for example. Said electric conduction material is formed from at least one sort chosen from a cobalt compound and metal cobalt. As said cobalt compound, 1 cobalt oxide, 3 oxidization 2 cobalt, cobalt hydroxide, etc. can be mentioned, for example. especially -- 1 cobalt oxide -- or the electric conduction material which consists of cobalt hydroxide is suitable.
[0013] As said binder, a carboxymethyl cellulose, methyl cellulose, sodium polyacrylate, polytetrafluoroethylene, etc. can be mentioned, for example.
[0014] The metal porous body of the shape of the shape of reticulated [which was formed as said conductive substrate from the metal with which nickel, stainless steel or nickel plating was performed, for example], and sponge, fibrous, or felt etc. can be mentioned.
[0015] 2) the paste type negative electrode 4 -- this negative electrode 4 prepares a paste by kneading under existence of water, after adding a binder and an electric conduction agent to hydrogen storing metal alloy powder, applies said paste to a conductive substrate, and after drying, it is manufactured by rolling out.
[0016] What is necessary is not to be restricted exceptionally, and to be able to carry out the occlusion of the hydrogen electrochemically generated in the electrolytic solution as said hydrogen storing metal alloy, and just to be able to emit the occlusion hydrogen easily at the time of discharge. For example, LaNi5 and MmNi5 (in Mm) Mean the misch metal which is the mixture of lanthanum system elements, such as La, Ce, Pr, Nd, and Sm. The thing of the thing of the multi-element system which permuted some of LnNi(s)5 (misch metal which carried out Ln; lanthanum enrichment), and these nickel by element like aluminum, Mn, Co, Ti, Cu, Zn, Zr, Cr, and B or a TiNi system, and a TiFe system can be mentioned. It is desirable to use the hydrogen storing metal alloy of the multi-element system expressed with a general formula LnNix Mny Az (however, the total value shows $4.8 <= x+y+z <= 5.4$, as for at least a kind of metal and atomic ratio x as which the misch metal which Ln becomes from La, Nd, Ce, and Pr, and A are chosen from aluminum and Co, and y and z) especially. The charge-and-discharge cycle life of the negative electrode containing such a hydrogen storing metal alloy of a rechargeable battery improves in order to control the pulverization accompanying progress of a charge-and-discharge cycle.
[0017] As for said binder, a mean molecular weight serves as [a mean molecular weight] polytetrafluoroethylene of the low molecular weight of 200,000-1 million from the polytetrafluoroethylene of the amount of giant molecules of 2 million-10 million, and other polymers.
[0018] As for a polymer besides the above, it is desirable to have the resistance over the alkali electrolytic solution. As this polymer, rubber system polymers, such as hydrophilic polymers, for example, a latex etc., such as polyacrylate, such as hydrophobic polymers (CMC), for example, a carboxymethyl cellulose, such as polyethylene and polypropylene, methyl cellulose (MC), and hydroxypropyl methylcellulose (HPMC) (SPA), for example, sodium polyacrylate etc., polyvinyl alcohol (PVA), and polyethylene oxide, polyacrylamide (PA), a polyvinyl pyrrolidone (PVP), polyethylene oxide (PEO), etc. can be mentioned, for example. It is desirable to use the mixed polymer which consists of polyacrylate and a carboxymethyl cellulose especially. Polyacrylate raises the distributed

stability of a paste. On the other hand, a carboxymethyl cellulose raises the adhesion to the conductive substrate of a paste.

[0019] Since it is hard to fibrose with the shearing stress to which the polytetrafluoroethylene of 200,000-1 million requires said mean molecular weight for said paste at the time of paste kneading, although a binding property is low, it has high water repellence. As for the addition of this polytetrafluoroethylene, it is desirable to make it the range of the 0.1 weight section - 2.1 weight section to said hydrogen storing metal alloy powder 100 weight section. This is based on the following reasons. When said addition becomes under the 0.1 weight section, the total amount of polytetrafluoroethylene becomes less than the 1.0 weight section, and there is a possibility that it may become difficult to improve the water repellence of said negative electrode. When said addition exceeds the 2.1 weight sections, there is a possibility that the alloy consistency of said hydrogen storing metal alloy may fall [the total amount of polytetrafluoroethylene] exceeding the 3.0 weight sections, and the capacity of said negative electrode may fall. The addition of the more desirable polytetrafluoroethylene of low molecular weight is the 1.0 weight section - 2.0 weight section to the hydrogen storing metal alloy powder 100 weight section.

[0020] Said mean molecular weight has high water repellence, while having a high binding property, in order that the polytetrafluoroethylene of 2 million-10 million may fibrose easily with the shearing stress applied to said paste at the time of paste kneading. As for the addition of this polytetrafluoroethylene, it is desirable to make it the range of the 0.9 weight section - 2.0 weight section to said hydrogen storing metal alloy powder 100 weight section. This is based on the following reasons. When said addition becomes under the 0.9 weight section, the reinforcement of said negative electrode falls and there is a possibility that hydrogen storing metal alloy powder may be omitted from said negative electrode at the time of a cell assembly. When said addition exceeds the 2.0 weight sections, in order for the fluidity of said paste and adhesiveness to fall, there is a possibility that the spreading nature to said conductive substrate of said paste may be spoiled. The addition of the more desirable polytetrafluoroethylene of the amount of giant molecules is the 1.0 weight section - 1.5 weight section to the hydrogen storing metal alloy powder 100 weight section.

[0021] It is desirable for a mean molecular weight to carry out 0.1 weight section -2.1 weight section addition of the polytetrafluoroethylene of 200,000-1 million to the hydrogen storing metal alloy powder 100 weight section at said paste, and for a mean molecular weight to carry out 0.9 weight section -2.0 weight section addition of the polytetrafluoroethylene of 2 million-10 million, and to make these total amounts into the 1.0 weight section - 3.0 weight section. Having limited the total amount of polytetrafluoroethylene to said range is based on the following reasons. When said total amount becomes under the 1.0 weight section, there is a possibility that it may become difficult to improve the water repellence of said negative electrode. On the other hand, when said total amount exceeds the 3.0 weight sections, in order for the alloy consistency of said hydrogen storing metal alloy to fall, there is a possibility that the capacity of said negative electrode may fall. It is still more desirable to carry out 0.5 weight section -2.0 weight section addition of the polytetrafluoroethylene of low molecular weight to the hydrogen storing metal alloy powder 100 weight section at said paste, and to carry out 1.0 weight section -1.5 weight section addition of the polytetrafluoroethylene of the

amount of giant molecules, and to make these total amounts into the 1.5 weight section - 2.5 weight section.
[0022] As for a polymer besides the above, it is desirable to carry out 0.015 weight section -2.0 weight section addition to the hydrogen storing metal alloy powder 100 weight section during a paste. This is based on the following reasons. There is a possibility that a possibility that it may become difficult to make stability distribute hydrogen storing metal alloy powder is during a paste when the addition of a polymer besides the above is made under into the 0.015 weight section, there may be a possibility that it may become difficult to make hydrogen storing metal alloy powder hold firmly to a charge collector, the paste which said roll turner dried more by the way further may exfoliate from a charge collector, and it may become impossible to produce a negative electrode. On the other hand, when the addition of a polymer besides the above exceeds the 2.0 weight sections, there is a possibility that the surface smoothness of the spreading side at the time of applying a paste to about [that improvement in the distributed stability of a paste and the holding power of hydrogen storing metal alloy powder cannot be desired] and a charge collector may be spoiled. The addition of other more desirable polymers is the 0.05 weight section - 1.0 weight section to the hydrogen storing metal alloy powder 100 weight section.
[0023] As for said electric conduction agent, specific surface area makes a subject the carbon black 700m2 / more than g. When said specific surface area is made into under 700m2 / g, there is a possibility that the flow of hydrogen storing metal alloy powder and a flow with hydrogen storing metal alloy powder and a conductive substrate may fall in said negative electrode. The range of a more desirable specific surface area is 800m2 / g-1300m2 / g.
[0024] As for the carbon black which has this specific surface area, it is desirable to have the three-dimensional chain structure formed when the carbon particle (primary particle) whose particle size is 10-30nm condensed secondarily. The negative electrode containing the carbon black which has this structure and specific surface area raises a flow with hydrogen storing metal alloy powder and a conductive substrate by leaps and bounds in the flow list of hydrogen storing metal alloy powder.
[0025] As said carbon black, it is desirable to use furnace black and KETCHIEN black. It is this class, and the negative electrode containing the carbon black which has the specific surface area of said range can improve negative-electrode capacity, and can improve the cell capacity of the rechargeable battery equipped with said negative electrode. Moreover, since the reactivity of the oxygen gas and the hydrogen storing metal alloy powder generated from a positive electrode can be improved when said rechargeable battery overcharges, it can control that cell internal pressure rises at the time of overcharge.
[0026] As for the blending ratio of coal of said electric conduction agent, it is desirable to consider as 0.1 weight section - 4 weight section to the hydrogen storing metal alloy powder 100 weight section. This is based on the following reasons. When the blending ratio of coal of said electric conduction agent is made under into the 0.1 weight section, there is a possibility that it may become difficult to fully attain the addition effectiveness of said electric conduction agent in said negative electrode. On the other hand, when the blending ratio of coal of said electric conduction agent exceeds 4 weight sections, the amount of hydrogen storing metal alloys per unit volume of said negative electrode decreases, and there is a possibility that large capacity may no longer be acquired. The

blending ratio of coal of a more desirable electric conduction agent is 0.1 weight section - 2 weight section to the hydrogen storing metal alloy powder 100 weight section.
[0027] As said conductive substrate, the thing of the three-dimensional structures, such as a thing of 2-dimensional structures, such as punched metal, an expanded metal, and a wire gauze, foaming metal, and a reticulated sintering metal fiber, etc. can be mentioned, for example.
[0028] 3) a separator 3 -- that by which hydrophilic processing was performed to the nonwoven fabric and the nonwoven fabric made from polyolefine system plastic fiber which consist of polyamide system plastic fiber (for example, nylon 6 and 6 fiber etc.) as this separator 3, for example can be mentioned. As said polyolefine, polyethylene, polypropylene, etc. can be mentioned, for example. Moreover, the approach of carrying out the graft copolymerization of the vinyl monomer which has plasma treatment, sulfonation processing, and a hydrophilic group, for example as said hydrophilic processing etc. can be mentioned. Especially the thing by which hydrophilic processing was performed to said nonwoven fabric made from polyolefine system plastic fiber has the high electrolytic-solution maintenance engine performance, and since oxidation resistance is excellent and the self-discharge at the time of elevated-temperature storage of said rechargeable battery is controlled, it is suitable.
[0029] 4) As the alkali electrolytic solution of alkali ********, the water solution of a sodium hydroxide (NaOH), the water solution of a lithium hydroxide (LiOH), the water solution of a potassium hydroxide (KOH), the mixed liquor of NaOH and LiOH, the mixed liquor of KOH and LiOH, the mixed liquor of KOH, LiOH, and NaOH, etc. can be used, for example.
[0030] In addition, although it applied to the cylindrical shape alkali rechargeable battery and being explained, it is applicable also like a square shape alkali rechargeable battery. Moreover, the electrode group contained in the container of said cell may make not only a spiral type but a positive electrode, a separator, and a negative electrode the gestalt which carried out two or more laminatings in this sequence.
[0031]
[Function] According to the alkali rechargeable battery of this invention, although it has high water repellence during the paste which constitutes a hydrogen storing metal alloy negative electrode, a mean molecular weight with the high binding property [the polytetrafluoroethylene of 200,000-1 million and a binding property] low mean molecular weight of a binding property contains the polytetrafluoroethylene of 2 million-10 million. A good fluidity is maintained and this paste has the outstanding spreading nature. For this reason, the negative electrode whose water repellence of the whole including the interior improved can be obtained by applying said paste to a conductive substrate.
[0032] Moreover, when specific surface area adds the carbon black 700m2 / more than g as an electric conduction agent during the paste of said negative electrode, a flow with hydrogen storing metal alloy powder and a conductive substrate can be made good at the flow list of the hydrogen storing metal alloy powder in said negative electrode. Consequently, in said negative electrode, hydrogen storing metal alloy powder is used efficiently, and since the surface area of the hydrogen storing metal alloy powder which participates in a charge-and-discharge reaction increases, the gas reaction rate of hydrogen storing metal alloy powder can be improved.

[0033] Therefore, since the hydrogen storing metal alloy powder of said negative electrode covers the whole, and a three-phase zone is formed and it has high gas reactivity, said negative electrode can absorb promptly the gas which occurs from a positive electrode at the time of overcharge and overdischarge. For this reason, it has the negative electrode which was produced more simply than the negative electrode with which the suspension of polytetrafluoroethylene was applied on the surface of the conventional method, and was excellent in the gas absorption engine performance, and the alkali rechargeable battery which can control internal pressure lifting at the time of overcharge can be offered. Furthermore, since said negative electrode has much surface area of the hydrogen storing metal alloy powder which participates in a charge-and-discharge reaction, it can offer the alkali rechargeable battery excellent in the high current discharge property.

[0034]

[Example] Hereafter, the example of this invention is explained to a detail with reference to a drawing.

an example 1 -- first -- LmNi4.2 Mn0.3 aluminum0.3 Co0.2 Before the activity, occlusion bleedoff of the gas hydrogen was carried out, pulverization was carried out, and the hydrogen storing metal alloy powder of 200-mesh pass was prepared. It continues. Specific surface area 0.5g and a carboxymethyl cellulose as 0.125g and electric conduction material for sodium polyacrylate to 100g of said hydrogen storing metal alloy powder by 700m2 / g After KETCHIEN black international incorporated company make and a trade name add 1.0g for the carbon black of the KETCHIEN black EC, A mean molecular weight the dispersion (specific gravity 1.28, solid content 40wt.%) of the low-molecular-weight polytetrafluoroethylene of 200,000-1 million 1.95ml (it is the 1.0 weight section by solid content conversion), The mean molecular weight added 1.11ml (it is the 1.0 weight section by solid content conversion), and 60ml of water, kneaded the amount polytetrafluoroethylene of giant molecules of 2 million-10 million (specific gravity 1.5, solid content 60wt.%) by the mixer, and the paste was prepared. The obtained paste was applied to the punched metal as a conductive substrate, and the negative electrode was produced by carrying out pressing with a roller press after desiccation at 80 degrees C.

[0035] To the mixed fine particles which consist of the 1 cobalt-oxide powder 10 weight section on the other hand as the nickel hydroxide powder 90 weight section which is an active material, and electric conduction material, as a binder, polytetrafluoroethylene 4 weight section addition was carried out, and the paste was prepared the carboxymethyl-cellulose 0.3 weight section, the sodium polyacrylate 0.3 weight section, and by carrying out 60 weight sections addition and kneading water to these. After continuing and being filled up with this paste in the nickel-plating fiber substrate as a conductive substrate, it dried and the paste type positive electrode was produced by casting.

[0036] The trial cel A shown in drawing 2 using the negative electrode and positive electrode which were obtained was assembled. That is, in the container 21, the alkali electrolytic solution 22 which consists of a KOH solution of 8 conventions is held. The electrode group 23 is produced by inserting a negative electrode 24 with the positive electrode 26 of two sheets through the separator 25 with which thickness consists of a nonwoven fabric made from a polyamide which is 0.2mm, and is contained in said container 21. Two presser-foot plates 27 are pinching said electrode group 23 in the

meantime. It is immersed in said alkali electrolytic solution 22 in said container 21 by the reference electrode 28.
The trial cel A shown in drawing 2 mentioned above with the same configuration as an example 1 was assembled except specific surface area having used KETCHIEN black international incorporated company make, and the trade name having used the carbon black (an addition being 1.0g to 100g of hydrogen storing metal alloys) of the KETCHIEN black EC by 800m2 / g as electric conduction material of example 2 negative electrode.
The trial cel A shown in drawing 2 mentioned above with the same configuration as an example 1 was assembled except specific surface area having used KETCHIEN black international incorporated company make, and the trade name having used the carbon black (an addition being 1.0g to 100g of hydrogen storing metal alloys) of the KETCHIEN black EC by 1300m2 / g as electric conduction material of example 3 negative electrode.
Except that specific surface area used acetylene black 1g of 40m2 / g as an electric conduction agent of example of comparison 1 negative electrode, it is the same configuration as an example 1, and the trial cel A shown in drawing 2 mentioned above was assembled.
[0037] About the trial cel A of the acquired examples 1-3 and the example 1 of a comparison, charge and discharge are repeated with a 150mA [per 1g of hydrogen storing metal alloys] current, change of the negative-electrode potential in discharge of 10 cycle eye is measured, and the result is shown in drawing 3 .
[0038] It turns out that the trial cel A of examples 1-3 can continue at a long period of time, and can keep high the potential of the negative electrode at the time of discharge so that clearly from drawing 3 . This is because the negative electrode produced from the paste containing the binder containing the polytetrafluoroethylene of the amount of giant molecules and the polytetrafluoroethylene of low molecular weight and the electric conduction agent which specific surface area becomes from the carbon black 700m2 / more than g was used.
[0039] On the other hand, the trial cel A of the example 1 of a comparison is understood that the potential of the negative electrode at the time of discharge is low compared with examples 1-3. Moreover, it wound spirally through the separator with which thickness consists of a nonwoven fabric made from a polyamide fiber which is 0.2mm between the negative electrode of the acquired examples 1-3 and the example 1 of a comparison, and said positive electrode, and the electrode group was produced. This electrode group was inserted in the space of AA size of the container made of acrylic resin which attached the pressure sensor, the electrolytic solution which becomes this space from the KOH solution of 8 conventions was poured in and obturated, and the trial cel B (capacity 1000mAh) as shown in drawing 4 was assembled.
[0040] That is, the trial cel B is equipped with the cell case which consists of a case body 31 made of said acrylic resin, and cap 32. The space 33 which has the same bore and same height as a metal vessel of a cell of AA size is formed in the core of said case body 31. Said electrode group 34 is contained by said space 33 interior, and the electrolytic solution is further held in it. On said case body 31, said cap 32 is being airtightly fixed with the bolt 37 and the nut 38 through the rubber sheet 35 and O ring 36. The pressure sensor 39 is attached in said cap 32. An end is attached in a negative electrode and, as for

the negative-electrode lead 40, the other end is drawn through between said rubber sheets 35 and said O rings 36. An end is attached in a positive electrode and, as for the positive-electrode lead 41, the other end is drawn through between said rubber sheets 35 and said O rings 36.

[0041] About the trial cel B of the acquired examples 1-3 and the example 1 of a comparison, after performing an initial charge with a 100mA current for 15 hours, it discharged to 0.8V with the current of 1A. Furthermore, after charging with the current of 1A for 1.5 hours, the charge and discharge which discharge to 0.8V with the current of 1A are repeated 50 times, the maximum internal pressure in the charge last stage of 50 cycle eye is measured, and the result is shown in a table 1. In addition, the opening condition for [as the quiescent time] 30 minutes was given between charge, discharge and discharge, and charge, respectively.

[0042]

[A table 1]

[0043] It turns out that the trial cel B of examples 1-3 can control internal pressure lifting accompanying progress of a charge-and-discharge cycle so that clearly from a table 1. Furthermore, the separator with which thickness consists of a nonwoven fabric made from a polyamide fiber which is 0.2mm was infixed between the negative electrode of the acquired examples 1-3 and the example 1 of a comparison, and said positive electrode, it wound spirally, and the electrode group was produced. By 1000mAh(s), the geometric capacity which has the structure shown in drawing 1 which contained and mentioned above the electrolytic solution which consists of such an electrode group, 7 Ns KOH, and 1-N LiOH in the closed-end cylindrical cup assembled the cylindrical shape nickel hydrogen rechargeable battery of AA size.

[0044] About the rechargeable battery of the acquired examples 1-3 and the example 1 of a comparison, after performing an initial charge with a 100mA current for 15 hours, it discharged to 0.8V with the current of 1A. Furthermore, after charging with the current of 1A for 1.5 hours, the charge and discharge which discharge to 0.8V with the current of 1A are repeated, the overcharge trial charged with the current of 1A in 30 cycle eye for 2 hours is performed, the cell internal pressure change to elapsed time is measured, and the result is shown in drawing 5 .

[0045] The rechargeable battery of examples 1-3 is understood that the internal pressure lifting width of face at the time of overcharge is small compared with the example 1 of a comparison so that clearly from drawing 5 . Even when hydrogen gas generated the improvement in such a gas absorption property of a negative electrode from said positive electrode not only at the time of overcharge but at the time of reverse charge, it was checked that the same effectiveness is attained.

To 100g of the same hydrogen storing metal alloy powder of a presentation as four to

example 8 examples 1-3, the specific surface area as 0.125g and electric conduction material 0.5g and a carboxymethyl cellulose for sodium polyacrylate by 1300m2 / g After KETCHIEN black international incorporated company make and a trade name add 1.0g for the carbon black of the KETCHIEN black EC, The suspension which the mean molecular weight mixed and prepared at a rate (rate to the hydrogen storing metal alloy powder 100 weight section) as the low-molecular-weight polytetrafluoroethylene and the mean molecular weight of 200,000-1 million show the amount polytetrafluoroethylene of giant molecules of 2 million-10 million in the following table 2, 60ml of water was added, it kneaded by the mixer, and the paste was prepared. The obtained paste was applied to the punched metal as a conductive substrate, and the negative electrode was produced by carrying out pressing with a roller press after desiccation at 80 degrees C.

[0046] It wound spirally through the separator with which thickness consists of a nonwoven fabric made from a polyamide fiber which is 0.2mm between the negative electrode and examples 1-3 which were acquired, and the same positive electrode, and the electrode group was produced. This electrode group was inserted in the space of AA size of the container made of acrylic resin which attached the pressure sensor, and the trial cel B (capacity 1000mAh) shown in drawing 4 which poured in, obturated and mentioned above the electrolytic solution which becomes this space from the KOH solution of 8 conventions was assembled.

The same negative electrode as examples 4-10 was manufactured except having used the suspension with which a mean molecular weight contains the amount polytetrafluoroethylene of giant molecules 1.5 weight section of 2 million-10 million as a binder of the conventional example negative electrode, 0.5g sodium polyacrylate, and a 0.125g carboxymethyl cellulose. It continued, and the suspension of the polytetrafluoroethylene of the amount of giant molecules was applied to the front face of said negative electrode, and it gave a water-repellent finish by drying.

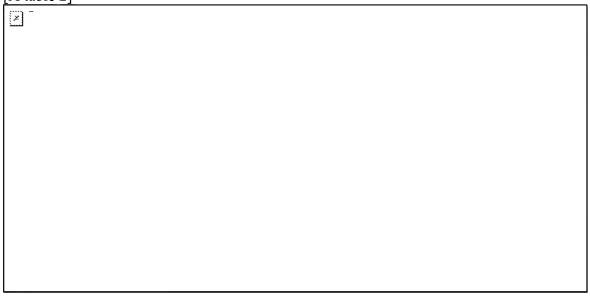
[0047] It wound spirally through the separator with which thickness consists of a nonwoven fabric made from a polyamide fiber which is 0.2mm between the negative electrode and examples 1-3 which were acquired, and the same positive electrode, and the electrode group was produced. This electrode group was inserted in the space of AA size of the container made of acrylic resin which attached the pressure sensor, and the trial cel B (capacity 1000mAh) shown in drawing 4 which poured in, obturated and mentioned above the electrolytic solution which becomes this space from the KOH solution of 8 conventions was assembled.

[0048] About the negative electrode of the acquired examples 4-8, the examples 2-5 of a comparison, and the conventional example, the spreading condition of a paste is investigated and the result is written together to the following table 2. Moreover, in case the spiral shape electrode group mentioned above is produced, it investigates whether hydrogen storing metal alloy powder exfoliated from these negative electrodes, and the result is written together to the following table 2.

[0049] Moreover, about the trial cel B of the acquired examples 4-8, the examples 2-5 of a comparison, and the conventional example, after charging 150% with the current of 0.3C, the charge-and-discharge cycle trial which discharges to 0.8V with the current of 1C is performed, the internal pressure of 50 cycle eye is measured, and the result is written together to the following table 2.

[0050]

[A table 2]



[0051] The negative electrode of examples 4-8 has the uniform fill of a paste, and since there is no exfoliation of the hydrogen storing metal alloy powder at the time of spiral shape electrode group production, it is understood that reinforcement is high so that clearly from a table 2. Moreover, it turns out that the trial cel B equipped with these negative electrodes can control internal pressure lifting accompanying progress of a charge-and-discharge cycle.

[0052] On the other hand, the trial cel B of the examples 3 and 5 of a comparison equipped with the negative electrode only containing PTFE of low molecular weight had many amounts of hydrogen storing metal alloy powder which dropped out, although the internal pressure of 50 cycle eye was comparatively low. On the other hand, there were many amounts of hydrogen storing metal alloy powder which the trial cel B of the example 2 of a comparison equipped with the little **** negative electrode had the high internal pressure of 50 cycle eye, and dropped out only PTFE of the amount of macromolecules. Moreover, since the paste which contains only PTFE of the amount of macromolecules so much like the example 4 of a comparison had too high viscosity, it was not able to be applied to the conductive substrate.

[0053] On the other hand, although the internal pressure of 50 cycle eye was low, the conventional example needed the activity which applies the suspension of polytetrafluoroethylene to a negative-electrode front face, and its manufacture of a negative electrode was complicated [the example].

To 100g of hydrogen storing metal alloy powder which has the same presentation as nine to example 12 examples 1-3, specific surface area 0.5g and a carboxymethyl cellulose as 0.125g and electric conduction material for sodium polyacrylate by 800m2 / g After KETCHIEN black international incorporated company make and a trade name add 0.1g, 1.0g, 2.0g, and 4.0g for the carbon black of the KETCHIEN black EC, A mean molecular weight the dispersion (specific gravity 1.28, solid content 40wt.%) of the low-molecular-weight polytetrafluoroethylene of 200,000-1 million 1.95ml, The mean molecular weight added 1.11ml and 60ml of water, kneaded the amount polytetrafluoroethylene of giant

molecules of 2 million-10 million (specific gravity 1.5, solid content 60wt.%) by the mixer, and the paste was prepared. The obtained paste was applied to the punched metal as a conductive substrate, and the negative electrode was produced by carrying out pressing with a roller press after desiccation at 80 degrees C.

[0054] It wound spirally through the separator with which thickness consists of a nonwoven fabric made from a polyamide fiber which is 0.2mm between the negative electrode and examples 1-3 which were acquired, and the same positive electrode, and the electrode group was produced. This electrode group was inserted in the space of AA size of the container made of acrylic resin which attached the pressure sensor, and the trial cel B (capacity 1000mAh) shown in drawing 4 which poured in, obturated and mentioned above the electrolytic solution which becomes this space from the KOH solution of 8 conventions was assembled.

[0055] About the trial cel B of the acquired examples 9-12, after performing an initial charge with a 100mA current for 15 hours, it discharged to 0.8V with the current of 1A. Furthermore, after charging with the current of 1A for 1.5 hours, the charge and discharge which discharge to 0.8V with the current of 1A are repeated 30 times, the electrical-potential-difference change at the time of discharging with the current of 5A in 30 cycle eye is measured, and the result is shown in drawing 6 . In addition, the opening condition for [as the quiescent time] 30 minutes was given between charge, discharge and discharge, and charge, respectively.

[0056] It turns out that the trial cel B of examples 9-12 is excellent in a high current discharge property so that clearly from drawing 6 . It turns out that especially the trial cel B of the examples 9-11 equipped with the 0.1 - 2.0 weight ****** negative electrode for the electric conduction agent to the hydrogen storing metal alloy powder 100 weight section excels the example 12 in the high current discharge property.

[0057]

[Effect of the Invention] As explained in full detail above, according to the alkali rechargeable battery of this invention, internal pressure lifting accompanying progress of a charge-and-discharge cycle can be controlled, a high current discharge property can be improved substantially, and the remarkable effectiveness that a negative electrode is producible by the easy approach is done so.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The perspective view showing the cylindrical shape alkali rechargeable battery concerning this invention.

[Drawing 2] The sectional view showing the trial cel A used in the examples 1-3 of this invention.

[Drawing 3] Property drawing showing change of the negative-electrode potential at the time of changing the electrode capacitance in the examples 1-3 of this invention.

[Drawing 4] The sectional view showing the trial cel B used in the examples 1-12 of this invention.

[Drawing 5] Property drawing showing aging of the cell internal pressure in the examples

1-3 of this invention.
[Drawing 6] Property drawing showing aging of the cell voltage in the examples 9-12 of this invention.
[Description of Notations]
1 [-- A negative electrode, 5 / -- An electrode group, 7 / -- An obturation plate, 8 / -- Insulating gasket.] -- A container, 2 -- A positive electrode, 3 -- A separator, 4